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FINAL REPORT

UNIVERSITY OF PITTSBURGH/YATES

AFOSR-86-0107

THE ORIENTATION OF CHEMICAL BONDS AT SURFACES - A KEY TO
UNDERSTANDING THE STRUCTURE AND BONDING OF SURFACE SPECIES

15 April 1986 - 14 April 1989

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19. ABSTRACT (Continue on reverse if necessary and identify by block number) This work has been concerned with the development and use of the digital ESDIAD method for studying the molecular structure and the dynamics of adsorbates on metal single crystal surfaces. A number of new findings have been made involving the following phenomena: (A) First direct observation of the hindered rotation of a chemisorbed molecule; (B) Observation of hydrogen bonding forces between adsorbates causing hinderance of molecular rotation; (C) Structural determination of bonding site for coordinatively unsaturated radical species, PF ₂ and PF on Ni(111). (This experimental result has just been verified by theoretical analysis by Dr Chen and Roald Hoffmann at Cornell); (D) Discovery of alkali metal sensitization of H ⁺ ESD yield on metals; (E) Discovery of copious metastable CO yield in ESD from CO on Pt(111). (This permits studies by ESDIAD in which no image potential effects exist); (F) Study of ESD-induced molecular fragmentation of an adsorbed					
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polyatomic species (CH₃O), using vibrational spectroscopy to follow species interconversion; (G) development of the symmetrization method for analysis of digital ESDIAD data; (H) Observation of tilting of adsorbates at high surface density; (I) Observation of a surface phase transition by changes in vibrational dynamics of the adsorbates; (J) Observation of adsorbate-adsorbate interactions along a 1 dimensional chain (on step sites); (K) Observation of anisotropic vibrational amplitudes for an adsorbate on a step site.

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University of Pittsburgh

DEPARTMENT OF CHEMISTRY
Surface Science Center

22 June 1989

Dr. Larry W. Burggraf, USAF
Program Manager
Directorate of Chemical and
Atmospheric Sciences
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Dear Larry,

I am submitting the final technical report covering our digital ESDIAD studies from 15 April 1986 to 14 April 1989, the final date of the contract.

During this period, 21 research and review papers under AFOSR support were written. I include a short overall summary of the work plus abstracts and references of the 21 papers which were produced.

I. Overall Summary

This work has been concerned with the development and use of the digital ESIDAD method for studying the molecular structure and the dynamics of adsorbates on metal single crystal surfaces. A number of new findings have been made involving the following phenomena:

Highlights of Digital ESDIAD Studies

- A. First direct observation of the hindered rotation of a chemisorbed molecule.
- B. Observation of hydrogen bonding forces between adsorbates causing hinderance of molecular rotation.

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- C. Structural determination of bonding site for coordinatively unsaturated radical species, PF_2 and PF on Ni(111) . (This experimental result has just been verified by theoretical analysis by Dr. Chen and Roald Hoffmann at Cornell.)
- D. Discovery of alkali metal sensitization of H^+ ESD yield on metals.
- E. Discovery of copious metastable CO yield in ESD from CO on Pt(111) . (This permits studies by ESDIAD in which no image potential effects exist.)
- F. Study of ESD-induced molecular fragmentation of an adsorbed polyatomic species (CH_3O), using vibrational spectroscopy to follow species interconversion.
- G. Development of the symmetrization method for analysis of digital ESDIAD data.
- H. Observation of tilting of adsorbates at high surface density.
- I. Observation of a surface phase transition by changes in vibrational dynamics of the adsorbates.
- J. Observation of adsorbate-adsorbate interactions along a 1 dimensional chain (on step sites).
- K. Observation of anisotropic vibrational amplitudes for an adsorbate on a step site.

II. Abstracts and References to the Work

MOLECULAR ORIENTATION ON METAL SURFACES BY ELECTROSTATIC INTERACTIONS - THE ADSORPTION OF CYCLOPENTENE ON A STEPPED (221) SILVER SURFACE, Mark D. Alvey, Kurt W. Kolasinski, and John T. Yates, Jr.

Abstract

Step defects at metal surfaces are known to cause a local dipole at the surface, thereby creating an enhanced surface electric field in their vicinity. Using the Electron Stimulated Desorption Ion Angular Distribution (ESDIAD) technique, cyclopent-

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tene is observed to be ordered by the interaction of its permanent dipole moment with the electrostatic field at the steps on the Ag(221) surface. This ordering is not seen for cyclopentene on Ag(111). The experimental results agree with estimates of the interactional energy of the dipole with the electric field at the steps, and the direction of orientation is consistent with calculations of the sign of the cyclopentene dipole moment.

J. Chem. Phys., 85, 6093 (1986)

ION ANGULAR DISTRIBUTION OF SPECIES DESORBED FROM SINGLE CRYSTAL SURFACES BY ELECTRON IMPACT, John T. Yates, Jr., Mark D. Alvey, Kurt W. Kolasinski and Miles J. Dresser

Abstract

The measurement of the angular distribution of desorbing positive ions produced by electron impact desorption (ESDIAD) is of fundamental importance in understanding molecular structure in the chemisorbed layer. In this short review, two applications of ESDIAD to structural problems in the adsorbed layer will be described. Examples of strong chemisorption and weaker physical adsorption effects will be discussed. In addition, interactions between adsorbed species, leading to changes in bonding geometry will be described. The apparatus used for this work allows digitized acquisition of ion angular distributions in the absence of background effects due to soft X-ray emission stimulated by electron impact.

Nuclear Instruments and Methods in Physics Research, B27, 147-154 (1987)

THE DIRECT OBSERVATION OF HINDERED ROTATION OF A CHEMISORBED MOLECULE: PF₃ ON Ni(111), Mark D. Alvey and John T. Yates, Jr. and Kevin J. Uram

Abstract

By using the bond direction imaging capabilities of the electron stimulated desorption ion angular distribution (ESDIAD) technique, we have observed a thermally induced azimuthal

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disorder effect due to the thermal population of unbound hindered rotor states in chemisorbed PF_3 on $\text{Ni}(111)$. The six beam F^* ESDIAD patterns observed for PF_3 on $\text{Ni}(111)$ are interpreted as evidence for a weak barrier that hinders the rotation of isolated PF_3 molecules on the $\text{Ni}(111)$ surface. At a coverage of ~ 0.04 PF_3/Ni , a barrier to rotation of $\sim 80 \text{ cm}^{-1} \pm 20 \text{ cm}^{-1}$ is estimated from the observed temperature dependence of the F^* ESDIAD patterns using a two-dimensional hindered rotor model. The PF_3 coverage dependence of the thermally induced azimuthal disorder effect indicates that intermolecular forces are responsible for an increase in the hindering potential at high PF_3 coverages.

J. Chem. Phys., 87(12), 7221 (1987)

INTERACTION BETWEEN NH_3 AND CO ON THE $\text{Ni}(111)$ AND (110) SURFACES:
A STUDY BY ESDIAD, Miles J. Dresser, Ann-Marie Lanzillotto, Mark
D. Alvey, and John T. Yates, Jr.

Abstract

The interaction between adsorbed NH_3 and adsorbed CO molecules on two Ni single crystal planes has been investigated using ESDIAD and temperature programmed desorption (TPD). Interactions have been observed on both surfaces which influence the ESDIAD patterns of both adsorbed species. Evidence for long distance azimuthal orientation interactions of NH_3 with CO on $\text{Ni}(110)$ is observed, whereas shorter distance interactions are observed on $\text{Ni}(111)$. In the case of the short distance $\text{CO} \cdots \text{NH}_3$ interactions on $\text{Ni}(111)$, a tipping of the C_3v axis of NH_3 away from the normal is seen. The role of the substrate crystal structure is shown to be important in determining the character of the intermolecular interactions on the two surfaces.

Surface Science, 191, 1 (1987)

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THE EPITAXIAL FORMATION OF ADSORBED MULTILAYERS AS STUDIED BY
ESDIAD: NH₃ ADSORPTION ON TOP OF CHEMISORBED CO ON NICKEL
CRYSTAL SURFACES, Ann-Marie Lanzillotto, Miles J. Dresser, Mark
D. Alvey, and John T. Yates, Jr.

Abstract

The epitaxial growth of an adsorbed layer of NH₃ on top of chemisorbed CO on Ni(111) and Ni(110) surfaces was studied using ESDIAD. A strong interaction yielding an activation energy for NH₃ desorption of ~12 kcal/mole was observed. This interaction, possibly involving hydrogen bonding, between the adsorbed NH₃ and adsorbed CO causes a tilting of the NH₃ molecules on the CO-covered Ni surfaces. For the NH₃/CO/Ni(110) system, the two-fold symmetry of the underlying Ni substrate is transmitted through the CO spacer layer to the NH₃ overlayer. This symmetry transfer was not observed for the NH₃/CO/Ni(111) system at the current resolution of our ESDIAD detection system.

Surface Science, 191, 15 (1987)

INTERACTIONAL EFFECTS IN THE CHEMISORBED LAYER, John T. Yates, Jr., M.D. Alvey, M.J. Dresser and A-M. Lanzillotto

Abstract

The digital ESDIAD technique for imaging chemical bond directions in chemisorbed molecules is discussed with application to the study of the hindering of molecular motions and the promotion of conformational changes in adsorbates due to inter-molecular forces at the surface.

Chemically Modified Surfaces in Science and Industry, Vol. 2, ed. by Donald Leyden and Ward T. Collins, Gordon & Breach Science Publishers, 1988, 239

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DIET IN THE SECOND LAYER: AN ESDIAD STUDY OF NH_3 ON A CO LAYER ON Ni(111) AND Ni(110), Miles J. Dresser, Ann-Marie Lanzillotto, Mark D. Alvey, and John T. Yates Jr.

No Abstract

Desorption Induced by Electronic Transitions DIET III, ed. by M. Knotek and R. Stulen, Springer Series in Surf. Sci., pg. 100 - 108, 1988

OBSERVATION OF MOLECULAR ROTORS ON SURFACES BY ESDIAD. STUDIES OF PF_3 AND NH_3 CHEMISORPTION ON Ni SURFACES, J.T. Yates, Jr., M.D. Alvey, M.J. Dresser, A-M. Lanzillotto and K.J. Uram

No Abstract

Desorption Induced by Electronic Transitions DIET III, ed. by M. Knotek and R. Stulen, Springer Series in Surf. Sci., pg. 115 - 119, 1988

THE STRUCTURE AND CHEMISTRY OF CHEMISORBED PF_3 , PF_2 AND PF ON Ni(111): AN ESDIAD STUDY, Mark D. Alvey and John T. Yates, Jr.

Abstract

The chemisorption of PF_3 on Ni(111) was studied with the electron stimulated desorption ion angular distribution (ESDIAD) technique, temperature programmed desorption (TPD), Auger electron spectroscopy (AES) and low energy electron diffraction (LEED). PF_3 is shown to bond to atop Ni sites, with PF bonds azimuthally oriented over neighboring Ni atoms. There are two such orientations on the Ni(111) surface that contribute to the observed six beam F^+ ESDIAD pattern. Also, $\text{PF}_3(\text{ads})$ dissociates under electron irradiation, producing the surface species $\text{PF}_2(\text{ads})$ and $\text{PF}(\text{ads})$. The PF_2 and PF species produce a F^+ ESDIAD

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pattern which indicates that PF_2 is bound to 2-fold bridge sites, and PF is bound so that the P-F bond is normal to the surface. The chemisorption bonding of PF_3 and PF_2 to $\text{Ni}(111)$ is in accordance with known modes of coordination of these ligands in transition metal complexes.

J. Am. Chem. Soc. 110, 1782 (1987)

ALKALI SENSITIZATION OF H^+ ELECTRON STIMULATED DESORPTION FROM H ADSORBED ON $\text{Ni}(111)$, A-M. Lanzillotto, M.J. Dresser, M.D. Alvey and J.T. Yates, Jr.

Abstract

It is shown that alkali adatoms coadsorbed in the presence of adsorbed hydrogen on $\text{Ni}(111)$ can cause a large increase in the cross section for H^+ emission during electron stimulated desorption. This phenomenon was investigated using the digital ESDIAD (electron stimulated desorption ion angular distribution) technique as well as by temperature programmed desorption (TPD). H^+ ions produced by electron impact on alkali-hydrogen complexes are ejected in sharp normally-oriented ion angular distributions.

e^-
The sensitization of the $\text{H(a)} + \text{H}^+$ process occurs with Li, Na and K but not as strongly with Rb and Cs. Attractive interactions exist in the adsorbed layer between the hydrogen and the alkali adatoms. A model is discussed involving the formation of "alkali-hydride-like" surface complexes, with H^0 located on top of alkali atom sites.

J. Chem. Phys., 89(1), 570 (1988)

THE ACTIVATION OF CHEMICAL BONDS AT SURFACES, John T. Yates, Jr.

No Abstract

Solvay Conference on Surface Science, G. Ertl, Editor, Springer Series in Surface Sciences, 14, 74 (1989)

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**ELECTRON STIMULATED DESORPTION FROM CO CHEMISORBED ON Pt(111)-
A DYNAMICAL STUDY OF POSITIVE ION AND METASTABLE CO EMISSION,
M. Kiskinova, A. Szabo, A-M. Lanzillotto, and J.T. Yates, Jr.**

Abstract

The desorption by electron impact of significant quantities of electronically excited neutral species, CO^* , from CO adsorbed on Pt(111) has been discovered. Comparison of the yield of this species as a function of electron energy, coverage, and temperature, with the yield of O^+ and CO^+ has led to the conclusion that the CO^* species is mainly produced by direct excitation. Studies of the angular distribution of the three ESD-derived species have been made as a function of temperature, and high amplitude bending vibrational modes are observed. Isotope effects in the three desorption channels have been measured.

Surface Science, 202, L559 (1988)

**FRAGMENTATION OF MOLECULAR ADSORBATES BY ELECTRON AND ION
BOMBARDMENT: METHOXY CHEMISTRY ON Al(111), P. Basu, J. G. Chen,
L. Ng, M. L. Colaianni, and J. T. Yates, Jr.**

Abstract

High Resolution Electron Energy Loss Spectroscopy (EELS) has been used successfully to provide direct spectroscopic evidence regarding details of the molecular fragmentation of methoxy (CH_3O) on Al(111) caused by energetic electron and ion beams. Chemisorbed methoxy on Al(111) is produced by heating of adsorbed CH_3OH . Irradiation of $\text{CH}_3\text{O}(\text{a})$ by either energetic (~ 300 eV) electrons or Ar^+ ions results in C-O and C-H bond scission with simultaneous formation of Al-O and Al-C bonds. During electron stimulated desorption the $\text{CH}_3\text{O}(\text{a})$ species undergo sequential fragmentation first to CH_x groups that are captured by the surface and in the final decay process to adsorbed carbon. C-O bonds in $\text{CH}_3\text{O}(\text{a})$ are depleted preferentially compared to C-H bonds in $\text{CH}_x(\text{a})$ species. The electron induced sequential fragmentation of the parent CH_3 group (from methoxy) to resultant $\text{CH}_x(\text{a})$ occurs with an efficiency ~ 3 orders of magnitude greater than the subsequent process of $\text{CH}_x(\text{a}) \rightarrow \text{C}(\text{a})$. Cross sections for

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various bond scission processes in electron and ion bombardment have been estimated.

J. Chem. Phys., 89(4), 406 (1988)

THE SYMMETRIZATION METHOD FOR ENHANCEMENT OF DIGITAL ESDIAD MEASUREMENTS- INCREASED RESOLUTION FOR STUDY OF ADSORBATE BOND DIRECTIONS, A. Szabó, M. Kiskinova and J.T. Yates, Jr.

Abstract

A new data smoothing method for distinguishing the symmetrical features of digital ESDIAD patterns has been developed. The method is based on the assumption that ESDIAD patterns from adsorbed molecules on an "n"-fold symmetric single crystal surface should in principle contain the same "n"-fold symmetry, although in some cases this may be below the detection limit. The symmetrization method is applied to real ESDIAD data with the expected enhancement of the azimuthal symmetry of the ESDIAD pattern. Two strenuous tests have been devised to determine the reliability of the method: (i) quantitative comparison of azimuthal symmetry elements in the digital ESDIAD pattern with the substrate symmetry as determined by digital LEED in the same apparatus; (ii) qualitative comparison of physically-meaningful symmetry elements with non-physical symmetries. It is also shown in model calculations that the symmetrization procedure is effective in removing systematic noise from digital ESDIAD data.

Surface Science, 205, 207 (1988)

COMPRESSED CO OVERLAYERS ON Pt(111)- EVIDENCE FOR TILTED CO SPECIES AT HIGH COVERAGES BY DIGITAL ESDIAD, M. Kiskinova, A. Szabo, and J.T. Yates, Jr.

Abstract

The existence of tilted CO molecules in compressed CO overlayers on Pt(111) has been detected using the digital ESDIAD method with enhanced resolution achieved by applying a retarding

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potential procedure to separate CO^+ , CO^* , and O^+ ESD products. Digital symmetrization was used for analysis of the ESDIAD data collected under field-free conditions. The CO tilting is consistent with the building of antiphase domain boundaries of close-packed terminal-CO species. It has been found that CO molecules tilt about 6° off-normal at CO coverages higher than 0.6 CO/Pt. The 6 azimuthal directions (equivalent to $\{110\}$) of CO tilting indicate that the close-packed CO molecules are repelled along the nearest Pt-Pt neighbor directions. Studies of the thermal broadening of the CO^+ ESDIAD patterns due to the tilted-CO molecules have shown that the maximum amplitude of the vibrational motion of the tilted-CO species occurs along the directions normal to the tilting plane. A comparison of the CO^+ and CO^* ESDIAD patterns has permitted approximate estimation of the distance of the image plane from the center of the charge for the CO^+ ESD product at the point of its origin.

Surface Science, 205, 215 (1988)

CO ADSORPTION ON Pt(111) MODIFIED WITH SULFUR, M. Kiskinova, A. Szabó, and J. T. Yates, Jr.

Abstract

CO adsorption on clean and S-covered Pt(111) is studied using temperature programmed desorption (TPD), electron stimulated desorption ion angular distribution (ESDIAD), LEED and work function measurements. Special attention is paid to comparing the CO adsorption rate, binding energy and soft bending modes on a clean surface and on $\text{p}(2 \times 2)\text{S}/\text{Pt}(111)$ with S coverage = 0.25 S/Pt. It was found that on $\text{p}(2 \times 2)$ 0.25 S/Pt(111) the CO adsorption rate is decreased by a factor of two and only one CO adsorption state with maximum coverage, $\theta_{\text{CO}} = 0.25$ CO/Pt is detected. On the basis of the ESD data the CO adsorption state on $\text{p}(2 \times 2)$ 0.25 S/Pt(111) is assigned to terminal-CO residing on the next nearest Pt atom and separated from S by 3.72 Å. When compared with the same CO configuration on clean Pt(111) in the limit of low θ_{CO} , the adsorption binding energy of the terminal CO on sulfided Pt(111) is decreased by 8 kcal/mole. For this same overlayer, the cross sections for production of all ESD products (CO^+ , O^+ , and metastable CO^*) is increased by 30 - 50 %. This result is interpreted considering the possible S-induced perturbations of the $\text{CO}-5\sigma/\text{metal}$ and $\text{metal}/\text{CO}-2\pi^*$ coupling. An

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important result in the present study is the observation of a substantial decrease of the polar angle of the ESDIAD patterns of all CO ESD products which indicates a decrease of the amplitude of the CO bending modes. This appears to be a direct experimental evidence for S-induced stiffening of the soft CO-bending vibrations. Approximate estimations (on the basis of the measured polar angles of the ESDIAD patterns) showed that the frequency of the CO wagging modes increases by about a factor of two - from 48 cm^{-1} for CO/Pt(111) to $\sim 100 \text{ cm}^{-1}$ for CO/p(2x2) 0.25 S/Pt(111).

J. Chem. Phys., 89(12), 7599 (1988)

OBSERVATION OF ADSORBATE VIBRATIONAL AMPLITUDE MODIFICATION
DURING A PHASE TRANSFORMATION IN THE OVERLAYER, Maya Kiskinova,
András Szabó, and John T. Yates, Jr.

Abstract

The digital ESDIAD method has been used to observe the amplitude of the low frequency "frustrated translational" modes of chemisorbed CO on Pt(111) when the CO adsorbs on empty Pt sites present in a p(2 x 2)-Se overlayer. Significant changes in the CO vibrational amplitudes are observed during a two-dimensional phase transition driven by repulsive forces in the overlayer. This work represents the first observation of the relationship between the vibrational amplitude of an adsorbed molecule and a phase transformation in an overlayer.

Phys. Rev. Lett., 61, 2875 (1988)

CARBON MONOXIDE-OXYGEN INTERACTION ON THE Pt(111) SURFACE - AN
ESDIAD STUDY, A. Szabo, M. Kiskinova and J.T. Yates, Jr.

Abstract

CO adsorption on the p(2x2)O-Pt(111) surface was studied by the digital ESDIAD (Electron Stimulated Desorption Ion Angular

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distribution) method in combination with TPD, LEED and work function measurements. Three ESD products were detected: CO^+ , O^+ and metastable CO. The ESDIAD patterns of each of these species were measured. The most significant difference in the ESD behavior of chemisorbed CO on the oxygen-covered surface from that of CO adsorbed on clean platinum surface was found at low CO coverages. This indicates that there is no preferential adsorption on the surface sites unaffected by oxygen. A small tilting of CO was found.

J. Chem. Phys. 90(8), 4604 (1989)

THE STRUCTURE OF CO ON THE Pt(112) STEPPED SURFACE - A SENSITIVE VIEW OF BONDING CONFIGURATIONS USING ELECTRON STIMULATED DESORPTION, M.A. Henderson, A. Szabó and J.T. Yates, Jr.

Abstract

The structure of chemisorbed CO on the steps of Pt(112) ($\text{Pt}[3(111)\times(001)]$) was monitored as a function of coverage by the digital electron stimulated desorption ion angular distribution method (ESDIAD), digital low energy electron diffraction (LEED) and temperature programmed desorption (TPD). The ESDIAD method applied to the desorption of an electronically excited, neutral CO species (the metastable $a^3\Pi$ -CO state) avoids the influence of image potential effects on the trajectory of desorbing species, yielding true desorption angles, equivalent to Pt-CO bond orientations. CO adsorbs exclusively on step sites at low coverage with a 20° "downstairs" tilt from the [112] direction (designated " 0° "). LEED indicates $(2 \times n)$ order (i.e. 2 fold order along the steps but no order up/down the steps) exists when the steps are half-filled (about 0.19 ML). At 0.24 ML, CO is still adsorbed only on the step sites but one - dimensional CO - CO repulsions between nearest neighbors result in CO tilting along the steps. Terrace CO ($+13^\circ$) adsorption is observed above 0.24 ML before all the step sites fill. All step CO molecules reorient with new tilt angles up (0°) and down (-38°) the steps when the steps sites saturate (0.53 ML), and (3×1) order is observed by LEED. The surface reorders at saturation (0.79 ML) to (2×1) order. Changes in CO desorption energies, preexponential factors and sticking coefficients with coverage in the literature for

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Pt[n(111)x(001)] surfaces can be directly correlated with structural transformations on the partially filled steps due to CO - CO repulsions.

J. Chem. Phys., submitted

DIRECT OBSERVATION OF ADSORBATE - ADSORBATE REPULSIONS ALONG A ONE - DIMENSIONAL ARRAY: CO ON THE STEPS OF Pt(112), M. A. Henderson, A. Szabó, and J. T. Yates, Jr.

Abstract

The orientation of CO on the steps of Pt(112) (Pt(S)[3(111)x(001)]) was studied by digital electron stimulated desorption - ion angular distribution (ESDIAD), monitoring the $\sigma^*-\text{CO}$ state. At low coverages, CO is adsorbed exclusively on step sites. At higher coverages, one - dimensional CO-CO repulsions result in tilting along the steps. When the steps are filled, all step CO molecules reorient orthogonally with new tilt angles up and down the steps. The selection of orthogonal tilt directions at various coverages has not been observed previously. These CO tilting effects are primarily due to steric repulsions rather than static dipole - dipole interactions.

Phys. Rev. Lett., submitted

DIRECT OBSERVATION OF ADSORBATE DYNAMICS FROM LOW FREQUENCY VIBRATION ON A STEP DEFECT - CO ON Pt(112), M. A. Henderson, A. Szabó and J. T. Yates, Jr.

Abstract

The relative shape of the hindered translation potential energy well for CO chemisorbed on the step sites of a Pt(112) single crystal was determined with digital electron stimulated desorption - ion angular distribution (ESDIAD). The angular displacement of the CO molecule in its hindered translation well predominately determines the half-width at half-maximum (HWHM) of

the neutral $a^3\pi$ CO species (CO^*) produced by ESD, a species which may be imaged in an ESDIAD apparatus. Variations in the CO^* ESDIAD HWHM as a function of temperature are due to population of higher levels of the hindered translational mode. By monitoring the CO^* ESDIAD HWHM for CO coverages on the step below 50% step saturation (0.17 ML) as a function of temperature, we show that the steepness of the hindered translation potential well is different for CO vibrations up, down and along the step edge, following the trend: down the steps > up the steps > along the steps. There is no coverage dependence in the CO^* ESDIAD HWHM values up or down the steps, but the HWHM values along the steps at 0.17 ML CO are significantly broader than those from lower coverages in the temperature range of 150 - 350 K. We interpret this to indicate the production of transient structures of tilted CO on adjacent step sites formed from preferential diffusion of CO molecules laterally on the step sites. Thus, the experiments probe directly the anisotropy of lateral diffusion of the adsorbate on step sites.

J. Chem. Phys., submitted

III. Concluding Remarks

We have developed and employed the digital ESDIAD method in a number of different types of studies involving both smooth and stepped single crystal metal surfaces. These results have given us both fundamental structural and dynamical information about interesting surface species, and evidence of the impact of these results (and earlier AFOSR-supported ESDIAD work) is now being seen in the scientific literature.

In addition to research publications, the program has produced in 3 years a total of 5 review papers resulting from invitations to discuss our work at major scientific meetings.

Our capability for doing digital ESDIAD studies paves the way for continued AFOSR-supported studies of tribological surface chemistry.


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The support of our work has also made major contributions to the training of two graduate students, one very outstanding undergraduate student, and four senior workers as listed below:

- M.D. Alvey Ph.D. (1987)
- A. Szabo Ph.D. expected (1991)
- K. Kolasinski B.S. (1986) - Now working for
 Professor R. Zare
 Stanford University
- Dr. A-M. Lanzillotto
- Professor M. Dresser
- Professor M. Kiskinova
- Dr. M. Henderson

We wish to express our deep thanks to AFOSR for the continued support of this work over a 7 year period. This support has been a major influence within my research group at Pittsburgh and has also been influential in a broader sense in the development of our understanding of surface phenomena.

Kind regards,



John T. Yates, Jr.
R.K. Mellon Professor of Chemistry
Director, Pittsburgh Surface Science Center

JTY/m